Thin Film Mediated Phase Change Phenomena: Crystallization, Evaporation and Wetting

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A microgravity environment can be obtained in a variety of different situations. The most dramatic is of course associated with space travel; the low gravity environment of the Moon, the parabolic flight of aircraft, or the free-fall of orbit, where large objects travel simple ballistic paths. The second environment is actually more familiar, lying in the molecular dynamics of fluids, gels, and other soft matter. In this latter case, gravitational influences are typically small compared to interfacial tension and other surface force effects. Our work embodies both of these settings.

We have focused on several areas. The first investigates that nature of crystallization of a two-component volatile liquid in a film configuration. This geometry is important for several reasons. In the limit that the film itself is thinner than the capillary length on earth, the dominant effects influencing the equilibrium configuration are surface energy and long- and short-range intermolecular interactions. These are particularly crucial near contact lines. However, as the film builds in thickness, the role of gravity becomes important in both equilibrium and nonequilibrium configurations. By parity of reasoning, as a thick film thins, for example by evaporation, the influence of gravity wanes. Finally, as gravity itself vanishes we can extend the spatial range over which surface energy and long range interactions influence the equilibrium and nonequilibrium behavior. We describe first the effect of evaporation in a pure film material and then examine the influence of a solute.

From the perspective of the bulk coexistence, the evaporation of a completely wetting one-component fluid might be considered as the reversible conjugate of the wetting process. However, as we showed earlier in the research program, attractive interactions with the substrate eliminate the reversibility by stabilizing thin films against a subsaturated vapor phase, wherein the subsaturation controls the equilibrium film thickness. A nucleation process initiated by the tails of the long range substrate potential ruptures the thick film and leaves the substrate covered by a uniform thin film which is in coexistence with the subsaturated vapor, but the thin film is decorated by droplets of evaporating fluid. These droplets stand at finite (macroscopic) contact angle and hence evaporation preempts the complete wetting of the substrate. The addition of another component to the fluid introduces an additional thermodynamic constraint, but furthermore dramatically changes the wettability and coating properties of the system. Experimental observations made on aqueous ammonium chloride by Prof. H. Stone and R. Du motivated a theoretical investigation of a model system that exhibits one of the primary features of the morphology of the experiments.

Consider a (incompletely wetting) droplet of solution standing on a substrate at finite contact angle. The species dependent volatility of the fluid drives crystallization during evaporation. Crystallization appears near the contact line of the droplet which drives the material over the substrate. The process involves a host of effects. In the thin-film limit, where diffusion dominates, we have found a crystallization instability which results in a highly nonuniform interface that is responsible for a spatially varying spreading process. The most dangerous mode is of zero wavenumber but the wavelength selection is weak, leaving us with the possibility of many modes manifesting themselves on the growth front. Hence, we have begun to understand why the observed contact line becomes so highly ramified.

As the initial value of the film thickness increases, two fluid mechanical phenomena become important and can therefore influence the evolution of the solidification front. The first is

Marangoni flow, driven by the variation of the surface tension with solute. In this case we have found a steady state similarity solution which is responsible for a variation in the film thickness with distance parallel to the solidification front. As the film thickens further, compositional convection, driven by the increased density of the fluid near the solid/vapor interface, may insue. We have identified the critical conditions for the onset of compositional convection in 1 g within the framework of the Oberbeck-Boussinesq equations. As gravity vanishes, the stability domain diverges. Therefore, we expect that in zero gravity the film thickness alone will determine the relative importance of diffusion and Marangoni convection in influencing the nature of the solidification instability.

The experimental component of our collaboration with Dr. M. Elbaum at the Weizmann Institute has taken advantage of new technology developed in the group and has been driven into an emerging area of microgravity materials. Although the continuum viscoelastic properties may be described without reference to the granular molecular nature, the relationship between the bulk rheology and the motions of the individual molecules which generates it is a matter of current research interest. Unfortunately it is not yet possible to image or trace the motion of single molecules at a scale relevant to the dynamics in ordinary materials, but we have exploited certain biopolymers in order to expand the scale of interest to that accessible by optical microscopy.

In an ideal simple liquid, molecules collide and diffuse in Brownian motion, driven by thermal energy. The path of an individual molecule is a trivial random walk in three dimensions, exploring points in space according to a simple diffusion law: the mean-square displacement is proportional to the time interval on which one observes. The assumption of ideality rests on the claim that each molecule acts independently in a randomizing field of all other molecules. They do not develop significant correlations, and in bulk they are described by simple Newtonian viscosity.

In the absence of gravity these effects will still be the same because the random collisions which thermalize the molecules impose a force much larger than that due to gravity. For an order of magnitude estimate, consider a molecule of molecular weight 1000 and typical diameter d=1 nm. The mass in kg is $1.0/N_A \sim 2 \times 10^{-24}$ kg. The force of gravity acting on the same length scale is $mgd \sim 2 \times 10^{-30}$ N. The typical Brownian force, by contrast, is of order the thermal energy at room temperature, divided by the length scale: $k_BT/d \sim 4 \times 10^{-12}$ N = 4 pN. Indeed, this comparison in favor of Brownian forces holds up to size scales approaching microns, as evident in the fact that non-aggregated colloidal suspensions do not sediment. The micron length scale is, however, accessible by light microscopy. Thus submicron particles are used as molecular tracers in the appropriate physical system.

We have studied individual polymer dynamics using a network of biopolymers called microtubules: polymerized forms of a protein called tubulin, which assembles into a hollow cylinder structure, 25 nm outer diameter and typically tens of microns in length. *In vivo*, microtubules exist within the cells of all animal and plant organisms, where they play structural, transport, and organizational roles. Their large diameter makes them far more rigid than ordinary polymers. The *persistence length* is on the scale of millimeters rather than nanometers. They remain sufficiently flexible, however, that thermal energy coupling into bending modes still produce measurable fluctuations. Individual microtubules were observed directly in the optical microscope using Nomarski differential interference contrast (DIC).

The mean-square displacement (MSD) of a free bead grows simply in proportion to the time interval. If the bead is bound to a microtubule, at the shortest time scales the diffusion of the bead displays the diffusional motion of the microtubule, primarily bending modes. The effect of thermally driven bending fluctuations on the MSD of an individual monomer leads to a predicted subdiffusion exponent. As the motion reaches saturation, we find that the persistence length is *shorter* than the actual length of the individual microtubules, and propose that the bead measures an

effective length representing the distance on which the microtubule interferes with its neighboring microtubules (i.e., the length on which its flexural fluctuations are inhibited laterally). These measurements were complemented by single-fiber experiments where a bead is attached to an isolated microtubule anchored at one end. In this way we compared the effects of the single fiber to those of the network.